CATALYST COMPRISING ZEOLITE BETA AND ITS USE IN HYDROCARBON CONVERSION PROCESS

TECHNICAL FIELD

This invention relates to the refining of petroleum hydro-
carbons into products of greater utility and higher value
5   as compared with the feedstock.

Conversion of hydrocarbons into useful products has been
practised for many years using catalytic materials. In re-
cent years, the use of catalysts containing zeolite materi-
10   als has been found in many cases to be superior to the
catalysts containing amorphous inorganic oxide materials
such as alumina, silica-alumina and the like. Many zeolitic
materials have been found to be useful as catalysts, but
depending on the specific process, zeolites such as Y, X,
15   omega, ZSM-5, beta and L have been found to be particularly
advantageous.
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This invention relates in general to catalytic compositions
useful for hydrocarbon conversion and in particular to
20   their use in hydrocarbon cracking reactions such as cata-
lytic cracking and hydrocracking. More particularly the in-
vention relates to compositions comprising certain zeolites
and metal hydrogenation components and their use in hy-
drocracking processes. In particular, the invention relates
25   to catalytic compositions comprising beta zeolite and a hy-
drogenation component and their use in hydrocracking of hy-
drocarbons. The invention moreover relates to the composi-
tion and use of catalytic compositions comprising specifi-
cally modified beta zeolites, which give enhanced perform-
30   ance in hydrocarbon conversion reactions especially in the
conversion of hydrocarbon feedstocks to middle distillates.

Often petroleum refiners produce desirable products, such
as gasoline and middle distillates, by catalytically hy-
drocracking high boiling hydrocarbons into product hydro-
carbons of lower average molecular weight and boiling

5   point. Hydrocracking is generally accomplished by contact-
ing in an appropriate reactor vessel a gas oil or other hy-
drocarbon feedstock with a suitable hydrocracking catalyst
under appropriate conditions including an elevated tempera-
ture and an elevated pressure and the presence of hydrogen,

10 such that a hydrocarbon product is obtained containing a
substantial portion of a desired product boiling in a
specified range, as for example a gasoline boiling in the
range of 85°C to 215°C or middle distillate boiling in the
range of 150°C to 425°C.

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Usually, hydrocracking is practised in a single reaction
vessel or several in series utilising a single catalyst. In
such a scenario, the catalyst not only hydrocracks the hy-
drocarbon feedstock but simultaneously or sequantially con-

20 verts the organonitrogen and organosulphur containing com-
pounds into ammonia and hydrogen sulphide. Some isomerisa-
tion of normal or near normal paraffins will also take
place simultaneously.

25 Hydrocracking can also be performed in conjunction with hy-
drotreating usually by a method referred to as "integral
operation". In this process, the hydrocarbon feedstock,
usually a gas oil containing a substantial proportion of
components boiling above a desired end point as for example

30 215°C in the case of certain gasolines, is introduced into
a catalytic hydrotreating zone wherein in the presence of a
suitable catalyst such as a zeolite or sieve-free, particu-

late catalyst comprising a Group VIII metal component and a
Group VIB metal component on a porous, inorganic, refrac-
tory oxide catalyst support most often composed of alumina,
and under suitable conditions including an elevated tem-
5   perature (e.g. 250°C to 540°C) and an elevated pressure
(e.g. 0.7 to 35 MPa) and with hydrogen as a reactant, the
organonitrogen components and the organosulphur components
contained in the feedstock are converted to ammonia and hy-
drogen sulphide, respectively. Subsequently, the entire ef-
10   fluent removed from the hydrotreating zone is treated in a
hydrocracking zone maintained under suitable conditions of
elevated temperature, pressure and hydrogen partial pres-
sure and containing a suitable hydrocracking catalyst, such
that a substantial conversion of high boiling feed compo-
15   nents to products components boiling below the desired end
point is obtained. Usually, the hydrotreating and hy-
drocracking zones in integral operation are maintained in
separate reactor vessels, but on occasion it may be advan-
tageous to employ a single, downflow reactor vessel con-
20   taining an upper bed of hydrotreating catalyst particles
and lower bed of hydrocracking particles. Examples of inte-
gral operation may be found in US Patent Nos. 3,132,087;
3,159,564; 3,655,551 and 4,040,944, all of which are herein
incorporated by reference in their entireties.

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When two catalysts in two separate vessels are used, it is
often desirable to fractionate (or separate) the products
of the first reactor (hydrotreating) so as to remove the
produced ammonia, hydrogen sulphide and light gaseous hy-
30   drocarbons from the feed to the hydrocracking reactor. Such
separation can also be made when two similar catalysts are
used.

In some integral operation refining processes, and espe-
cially those designed to produce gasoline from the heavier
gas oils, a relatively high proportion of the product hy-
drocarbons obtained from integral operation will have a
5   boiling point above the desired end point. For example, in
the production of a gasoline product boiling in the C_4 to
215°C range from a gas oil boiling entirely above 300°C, it
may often be the case that as much as 30 to 60 percent by
volume of the products obtained from integral operation
10   boil above 215°C. To convert these high boiling components
to hydrocarbon components boiling below 215°C, the petro-
leum refiner separates the 215°C+ high boiling components
from the other products obtained in integral operation usu-
ally after first removing ammonia by a water washing opera-
15   tion, a hydrogen-containing recycle gas by high pressure
separation, and an H_2S-containing C_1 to C_3 low BTU gas by
low pressure separation. This 215°C+ boiling bottom frac-
tion is then subjected to further hydrocracking either by
recycle to the hydrocracking reactor in single stage opera-
20   tion or by introduction into a second hydrocracking zone
wherein yet more conversion to the desired C_4 to 215°C
product takes place.

In the foregoing two stage process, the two hydrocracking
25   reaction zones often contain hydrocracking catalysts of the
same composition. One catalyst suitable for such use is
disclosed as Catalyst A in Example 16 of US Patent Nos.
3,897,327 and 3,929,672, both of which are herein incorpo-
rated by reference in their entireties, which catalyst is
30   comprised of a palladium-exchanged, steam-stabilised Y zeo-
lite hydrocracking component. But although the catalysts
used in the two hydrocracking reaction zones may have the

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same composition and the same catalytic properties, the hy-
drocracking conditions required in the second hydrocracking
reaction zone are less severe than those required in the
first. The reason for this is that ammonia is not present
5   in the second hydrocracking reaction zone (due to water
washing) whereas a significant amount of ammonia is present
in the first hydrocracking zone. To account for the differ-
ence in operating conditions, it is believed that ammonia
neutralises or otherwise interferes with the acidity of the
10   zeolite in the catalyst of the first reaction zone, thereby
forcing the refiner to employ relatively severe conditions
for operation as for example increased temperature. On the
other hand, in the ammonia-deficient atmosphere of the sec-
ond hydrocracking reaction zone, high conversions to the
15   desired product are obtainable under relatively moderate
conditions often with an operating temperature about 50°C
to 110°C lower than that required in the first hydrocrack-
ing reaction zone.

20   Further description of two-stage hydrocracking operations
may be found in US Patent Nos. 4,429,053 and 4,857,169
herein incorporated by reference in their entireties, which
patents provide process flow sheets for typical two-stage
hydrocracking processes.
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Although there exist several types of commercial hy-
drocracking catalysts, which can be used effectively in
single stage hydrocracking or either the first, second or
both stages of the above-discussed two-stage hydrocracking
30   process, there is always a demand for new catalysts with
superior overall activity, selectivity and stability for

6

producing gasoline and/or middle distillate via hydrocrack-
ing.

The general object of the present invention is directed to
novel catalysts and catalyst supports and novel acid cata-
lysed chemical conversion processes employing such cata-
lysts to promote the desired reactions. The present inven-
tion is particularly directed to hydrocarbon conversion
catalysts and hydrocarbon conversion processes employing
such catalysts comprising a hydrogenation component(s) on a
catalyst support comprising zeolite beta modified to a spe-
cific acidity.

SUMMARY OF THE INVENTION

The present invention provides a composition for use in the
acid catalysed chemical conversion of feedstocks containing
organic compounds into reaction products, particularly in
the acid catalysed conversion of hydrocarbons and most es-
pecially in hydrocracking. The composition, which may be a
catalyst and/or catalyst support, comprises a modified zeo-
lite beta. One or more amorphous, inorganic refractory ox-
ides such as alumina, silica-alumina or other inorganic ox-
ides may also be present in the composition. For hydro-
cracking purposes, the catalyst requires a hydrogenation
component such as one or more Group VIB and/or Group VIII
metal components, the hydrogenation components generally
being dispersed on the catalyst support material composed
of the zeolite beta and amorphous oxides.

7

The catalysts of the invention are characterised specifi-
cally by having a catalyst support with an NH_3-AI less than
3.5 and/or an IEC-AI less than 3.7.

5   DETAILED DESCRIPTION OF THE INVENTION

Zeolite beta is a crystalline zeolite whose composition and
X-ray powder diffraction analysis are disclosed in US Pat-
ent No. Reissue 28,341, herein incorporated by reference in
10   its entirety. This zeolite beta is a large pore zeolite
having a pore size above 7.0 Angstroms and a Constraint In-
dex below 2, preferably between 0.6 and 1.0. The Constraint
Index of a zeolite is a convenient measure of the extent to
which a zeolite provides access to molecules of varying
15   sizes to its internal structure. Zeolites, which provide a
highly restricted access to and egress from its internal
structure have a high value for the Constraint Index, and
zeolites of this kind usually have pores of small size. On
the other hand, zeolites, which provide relatively free ac-
20   cess to the internal zeolite structure, have a low value
for the Constraint Index. The method by which Constraint
Index is determined is described fully in US Patent No.
4,016,218, the disclosure of which is herein incorporated
by reference in its entirety.

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Procedures for measuring the acidity of a zeolite by NH_3
TPD and ion exchange capacity have been disclosed in US
Patent No. 4,894,142 to Steigleder and US Patent No.
4,612,108 to Bezman et al., all of which are herein incor-
30   porated by reference in their entireties. Temperature-
programmed desorption of ammonia (NH_3 TPD) is widely used
and is considered to be an effective procedure for deter-

8 .

mining the acidity strength of zeolites. Ion exchange ca-
pacity or IEC is intended to denote the number of active
cation sites (acidity) in the zeolite.

5   Zeolite beta is prepared, in general, as an aluminosilicate
zeolite having a SiO_2: Al_2O_3 molar ratio of at least 10. The
zeolite betas have a crystal size of about 0.1 to 5 micron,
a surface area of about 400 to 800, a cyclohexane adsorp-
tion capacity above 15 g/100 g and a water vapour sorptive
10   capacity at 25°C and a p/p_o value of 0.10 of greater than 5
weight percent. As used herein "p/p_o" represents the water
vapour partial pressure to which the zeolite beta is ex-
posed divided by the water vapour partial pressure at 25°C.

15   Preparation of zeolite beta has been disclosed in US Patent
Reissue No. 28,341. Standard preparation of zeolite beta
having a SiO_2:Al_2O_3 molar ratio of 25-30 have been described
in the 2nd revised edition of "Verified Syntheses of Zeoli-
tic Materials" by H. Robson (Editor) and K.P. Lillerud (XRD
20   Patterns), Elsevier 2001, which is herein incorporated by
reference in its entirety. Zeolite beta can be obtained
commercially from companies like Tosoh Corporation, Japan
or Zeolyst International, The Netherlands or Süd-Chemie AG,
Germany.

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As initially prepared, zeolite beta is usually in the al-
kali metal form and contains an organic templating agent.
In this form, the zeolite has low if any catalytic activity
for promoting acid catalysed conversion reactions, e.g.
30   cracking reactions. Accordingly, the zeolite is generally
converted to more active forms by calcination to decompose
and drive off the templating agent followed by base ex-

change with ammonium cations to substantially reduce the alkali metal content finally followed by another calcination to convert the ammonium-exchanged zeolite to the hydrogen form. For zeolite beta initially prepared in the sodium form, the preferred sodium content upon conversion to an active form is below 1.0 percent by anhydrous weight, preferably below about 0.5 percent by anhydrous weight, calculated as Na_2O.

Publications which further discuss the properties of zeolite Beta include US Patent Nos. 3,923,641; 4,676,887; 4,812,223; 4,486,296; 4,601,993 and 4,612,108, all of which are herein incorporated by reference in their entireties.

In accordance with the invention, it has now surprisingly been found that catalysts containing a metal hydrogenation component and certain modified zeolite beta with a certain ion exchange capacity acidity index and NH_3 TPD acidity index are significantly more selective for the production of middle distillate than comparable Y zeolites which for many years have and still form the component of choice in many hydrocracking catalysts.

The use of beta zeolite in hydrocracking catalysts has been reported over several years although there appears to be little if any commercial exploitation.

In US Patent No. 3,923,641 Morrison reported hydrocracking of C_5 naphtha into C_4 hydrocarbons using zeolite beta. Gas oil feeds are not contemplated as feedstocks and no attention is given to middle distillate. No mention of dealumination or $SiO_2:Al_2O_3$ molar ratio is made. Furthermore, no

mention of zeolite NH_3 TPD or ion exchange capacity is
made.

US Patent No. 5,128,024 to La Pierre discloses beta zeolite
containing catalyst with a $SiO_2:Al_2O_3$ molar ratio up to
280:1 for simultaneous hydrocracking and dewaxing. US Pat-
ent No. 5,980,859 to Gajda et al. discloses the modifica-
tion of beta zeolite by steaming and extraction with ammo-
nium nitrate by ion exchange. The modified zeolite is char-
acterised by IR spectroscopy. No measurements of the NH_3
TPD or IEC are reported. The disclosure lists uses for hy-
drocracking, catalytic cracking, isomerisation, transal-
kylation and alkylation although only its use for alkyla-
tion and transalkylation is illustrated. No relationship of
performance and acidity is disclosed and no specific refer-
ence to hydrocracking is made. The use is specifically di-
rected to benzene alkylation.

US Patent No. 5,972,832 to Shi et al. discloses a hy-
drocracking catalyst containing nickel, tungsten, fluoride,
a zeolite and alumina. The carrier contains 10-90% of a
zeolite which has an acidic strength value of 1.0-2.0 m
mole/g determined by ammonia TPD. Faujasite (Y), mordenite,
ZSM-5 and omega zeolite are specified. No acidity strength
of beta zeolite is reported. No variation of the zeolite
acidity is reported for the same family and no acidity of
the catalyst is reported. No dependence of the hydrocrack-
ing activity and selectivity on acidity and ion exchange
capacity is reported. No illustration of the utilisation of
beta zeolite or its comparative performance in hydrocrack-
ing is illustrated. Furthermore, no disclosure of ion ex-
change capacity is given.

11

US Patent No. 5,284,573 to La Pierre et al. discloses the
use of beta zeolite with a $SiO_2:Al_2O_3$ molar ratio of at
least 50 and even at least 250. A ratio of 500:1 may be
used. A process for hydrotreating and hydrocracking is

5   claimed. However, no disclosure of NH_3 TPD or ion exchange
capacity is made.

US Patent No. 4,612,108 to Angevine et al. discloses hy-
drocracking with beta zeolite directed to middle distillate

10   selectivity. The disclosure illustrates an improvement by
using a graded bed in which the concentration of beta zeo-
lite in the catalyst increases with bed depth. Although
$SiO_2:Al_2O_3$ molar ratio of the beta zeolite greater than 30
is disclosed, no properties of the zeolite containing cata-

15   lyst are given. No NH_3 TPD or ion exchange capacity data
are disclosed.

US Patent No. 4,401,556 to Bezman et al. discloses the use
of Y zeolite catalysts for hydrocracking in which the zeo-

20   lite has a preferred ion exchange capacity (IEC) no greater
than 0.07. No impact of IEC on hydrocracking activity is
reported, no NH_3 TPD is reported and no disclosure of beta
zeolite is made.

25   US Patent No. 4,894,142 to Steigleder discloses Y zeolites
with a NH_3 TPD of less than about 2.0 mmole/g, preferably
less than 1.5 mmole/g. It states that the selectivity of
the modified Y zeolite to produce middle distillate corre-
lates to the acid strength (Col 4 and Col 5). The acid

30   strength is measured by the NH_3 TPD value. The patent
teaches how to reduce the acid strength by calcination in
dry air. TPD NH_3 values <2.0 mmole/g and preferably <1.50

mmole/g are taught along with an IEC of >0.07 defined in US
Patent No. 4,401,556. No mention of beta zeolite is made.

5 .   US Patent No. 4,820,402 to Partridge et al. discloses the
use of zeolite beta for hydrocracking with $SiO_2:Al_2O_3$ molar
ratio up to 200 for producing high boiling distillate prod-
ucts. No reference to IEC or NH_3 TPD is made. The data il-
lustrate a continuous change in distillate selectivity with
the $SiO_2:Al_2O_3$ molar ratio for a range of zeolites such as
10   Y, ZSM-5, beta and ZSM-20. No differentiation between beta
and Y with $SiO_2:Al_2O_3$ molar ratio is disclosed. In fact a
smooth correlation exists for $SiO_2:Al_2O_3$ molar ratios from 3
to 300 suggesting that the $SiO_2:Al_2O_3$ molar ratio is domi-
nating. Large pore zeolites with $SiO_2:Al_2O_3$ molar ratios of
15   200:1 are said to give good middle distillate selectivi-
ties. No reference to IEC or NH_3 TPD is made.

DISCLOSURE OF INVENTION

20   The present invention is specifically directed to catalysts
and catalyst support comprising beta zeolites which have
been modified so that the NH_3 TPD acidity index (NH_3-AI) of
the catalyst support is less than 3.5 and preferably less
than about 2.3. The zeolite beta has also been modified so
25   that the IEC acidity index (IEC-AI) of the catalyst support
is less than 3.7, preferably less than about 2.7. The acid-
ity indices NH_3-AI and IEC-AI are defined in the section
covering the examples.

30   A synthesised beta zeolite can be modified by any known
method or other method which results in a decrease in NH_3
TPD and IEC of the original zeolite to one within the scope

13

of the invention. Many such methods for producing modified
zeolites have been reported.

Publications, which further discuss the properties of beta
5   zeolite, include US Patent Nos. 3,923,641; 4,676,887;
4,812,223; 4,486,296; 4,601,993 and 4,612,108. Specific il-
lustrations of beta zeolite modifications can be found in
the patent literature. Illustrative treatments of beta zeo-
lite to produce higher $SiO_2:Al_2O_3$ molar ratio can be found
10   in for example US Patent No. 4,820,402 (Partridge et al.)
and US Patent No. 4,430,516 (La Pierre et al.) who teach
various treatments illustrated by extraction, hydrothermal
treatment and ion exchange. Other methods involving direct
synthesis have been described in e.g. US Patent No.
15   5,554,356 to Saxton et al., US Patent No. 5,164,170 to Ru-
bin. US Patent No. 4,923,690 to Valyocsik describes a
method of synthesising beta zeolite which directly produce
higher $SiO_2:Al_2O_3$ molar ratio than those originally dis-
closed in US Patent No. 3,308,069 (Wadinger). All of these
20   patent disclosures are incorporated by reference in their
entireties.

Although the modified beta zeolite is the key component of
this invention, the catalyst or catalyst support will gen-
25   erally comprise the modified zeolite intimately mixed with
an acidic amorphous component and optimally a binder. The
amorphous inorganic oxide can be chosen from the well known
acidic oxides such as alumina, silica, titania, magnesia,
zirconia, boria, phosphorous oxides along with combinations
30   and the like. The composition of the catalyst support may
contain from about 0.5 to 50 wt% modified zeolite beta

14

preferably 1 to 30 wt% and more preferably 1 to 15 wt%
modified zeolite beta.

The $SiO_2:Al_2O_3$ molar ratio of the modified (M) zeolite beta
5   should be at least 50 and more preferably 100.

The modified zeolite beta and amorphous component required
in the catalyst and catalyst support of the invention are
embodied into particles which contain both components. Per-
10   haps the most convenient method for physically integrating
the two components into individual particulates is to
comull a wetted mixture of the components and then extrude
the comulled material through a die having small openings
therein of desired cross-sectional size and shape, e.g.
15   circle, trilobal clover-leaf, quadrolobal clover leafs
etc., breaking or cutting the extruded matter into appro-
priate lengths, drying the extrudates and then calcining at
a temperature, e.g. 480°C, or higher to produce a material
suitable for use in high temperature chemical conversion
20   reactions. At present it is preferred that the catalyst be
produced in cylindrical form, however, as stated above
other cross-sectional shapes are possible such as clover-
leafs of polylobal design, for example trilobal or
quadrolobal shapes, as shown for example in Figs. 8 and 10,
25   respectively, in US Patent No. 4,028,227 herein incorpo-
rated by reference in its entirety. Typically, the amor-
phous oxides besides contributing to the catalytic proper-
ties of the catalyst support also serve as a binder for the
modified zeolite beta. Alumina and other conventional amor-
30   phous, inorganic refractory oxide binder components may be
desired.

Regardless of whether an amorphous, inorganic refractory
oxide component is used as a binder material to hold the
zeolite beta and amorphous oxides together in the catalyst
support, it will be understood that other such components
5   can also be incorporated into the comulled mixture includ-
ing for example inorganic refractory oxide diluents, which
may or may not possess some type of catalyst activity. Ex-
amples of such diluents include clays, alumina, silica-
alumina and a heterogeneous dispersion of finely divided
10   silica-alumina particles in an alumina matrix, which dis-
persion is described in detail in US Patent Nos. 4,097,365;
4,419,271 and 4,857,171, the disclosures of which are
herein incorporated by reference in their entireties. Addi-
tionally and alternatively, hydrogenation component precur-
15   sors can also be comulled into the mixture, as will be dis-
cussed in more detail hereinafter.

It will be further understood that producing the catalyst
and catalyst support of the invention in extrudate form,
20   while certainly the most highly preferred method is still
but one option available to those skilled in the art. The
catalyst and its support may also be produced in tablet,
granules, spheres, and pellets as desired, by any known
method for combining zeolites with a porous, inorganic re-
25   fractory oxide component.

The catalyst of the invention can be used for converting
hydrocarbons and other organic compounds into more valuable
reaction products by acid catalysed reactions such as alky-
30   lation, transalkylation, dealkylation, isomerisation, dehy-
drocyclisation, dehydrogenation, hydrogenation, cracking,
hydrocracking, dewaxing, hydrodewaxing, oligomerisation,

aromatisation, alcohol conversion reactions, the conversion
of syngas into mixtures of hydrocarbons and the like. When
the catalyst or catalyst support contains modified zeolite
beta but no hydrogenation components, it is useful for any
5   of a number of acid-catalysed hydrocarbon conversion reac-
tions in which hydrogen is not an added reactant, e.g. iso-
merisation, alkylation, transalkylation, cracking, dewax-
ing, oligomerisation etc. However, since the main benefit
of the invention as presently contemplated is in hydroproc-
10   essing such as hydrocracking, a process in which hydrogen
is an added reactant, the catalyst for this purpose will
further require one or more hydrogenation components, in
which case the portion of the catalyst exclusive of any hy-
drogenation metal components is considered the catalyst
15   support upon which the hydrogenation component(s) is dis-
persed.

Whether the modified zeolite beta particulates, which may
optionally include an inorganic refractory oxide binder
20   and/or diluent, are used as the catalyst itself or as the
catalyst support (or support component) for hydrogenation
metals, the amounts of the modified zeolite beta and other
components present will normally depend on the particular
process in which the particles are used.

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When the modified zeolite beta particulates are used for
selectively producing middle distillates in a hydrocracking
process, the catalyst support will typically on a dry basis
contain less than 50 wt%, preferably less than 30 wt% and
30   more preferably less than 15 wt% modified zeolite beta with
at least 50 wt%, preferably 100 wt% of the balance being an

17

amorphous, inorganic refractory oxide binder and diluent in
combination.

For use in hydroprocessing, such as hydrocracking, the
5   catalyst contains one or more hydrogenation components con-
taining metals selected from the group consisting of Group
VIB and/or Group VIII of the periodic table of elements,
such components typically being in the form of the free
metals or their respective oxides and sulphides the latter
10   two being most preferred. As used herein "Periodic Table of
Elements" refers to the version found in the inside front
cover of the "Handbook of Chemistry and Physics", 59th Edi-
tion, published in 1979 by the Chemical Rubber Company. The
platinum group (or noble) metals of the Group VIII metals
15   may be used, but preference is at present for the base (or
non-noble) metals, e.g. nickel and cobalt in particular,
and nickel most preferably of all. Of the group VIB metals,
molybdenum and tungsten are preferred with molybdenum being
most preferred when the catalyst is to be used in gasoline
20   hydrocracking and tungsten being most preferred when the
catalyst is to be used in middle distillate hydrocracking.
The most highly preferred catalyst contains both a non-
noble Group VIII metal component and a Group VIB metal com-
ponent, most preferably nickel and molybdenum or nickel and
25   tungsten in combination.

The hydrocracking catalysts of the invention contain at
least 0.2 wt% of the hydrogenation components calculated as
the metals. If noble metals are used, the hydrogenation
30   components are generally present in a relatively low pro-
portion, e.g. 0.2 to 2 wt%. For the base or non-noble met-
als, the proportions are generally higher. Non-noble Group

VIII metal components are typically employed in proportions
between about 2 and 15 wt%, preferably between 3 and 10
wt%, calculated as the respective monoxide. The Group VIB
metal component is generally employed in proportions of

5   about 5 to 35 wt%, preferably in the range of 8 to 30 wt%,
calculated as the respective trioxide. It is to be under-
stood that the proportions given above for the hydrogena-
tion metal components are based on the finished catalyst
whereas the proportions expressed above for the modified

10 zeolite beta particulates are values in the absence of the
hydrogenation metal component, i.e. for the catalyst sup-
port only. For purposes herein, the term "catalyst support"
is defined as all materials in the catalyst except the hy-
drogenation metal components.

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The hydrogenation components may be incorporated into the
catalyst in any of many ways known in the art of combining
hydrogenation components with catalyst supports containing
zeolites. One such method is to first prepare the catalyst

20 support, for example, as an extrudate containing zeolite
beta and an amorphous inorganic refractory oxide in cal-
cined form and then impregnating the catalyst support with
solutions containing the desired metal(s) in dissolved
form. Calcination in air, typically in the absence of added

25 steam at an elevated temperature, e.g. above 425°C, pref-
erably above 475°C, produces the desired catalyst contain-
ing metals in oxide form. Likewise, in another embodiment,
the desired metal(s) are introduced by comulling a compound
containing such metal(s) in the zeolite beta amorphous ox-

30 ide mixture previously described followed by shaping (e.g.
extrusion through a die), drying and calcining in the sub-
stantial absence of steam, e.g. at a temperature between

19

about 425° and 550°C to produce the oxide form of the cata-
lyst. For one preferred catalyst, the comulling is effected
with ammonium heptamolybdate as the source of molybdenum
and nickel nitrate as the source of nickel with both com-
pounds generally being introduced into the mulling mixture
in the form of an aqueous solution. Other metals can be
similarly introduced in dissolved aqueous form likewise,
non-metallic elements, e.g. phosphorus.

Catalysts, which contain hydrogenation components in the
oxide form as described above, are generally treated to
convert the metals to the sulphide form prior to the use of
the catalysts in hydrocracking. This can be accomplished by
presulphiding the catalyst prior to use at an elevated tem-
perature, e.g. 150 to 375°C with for example a mixture con-
sisting of 10 volume percent H_2S and 90 volume percent H_2.
Alternatively, the catalyst can be presulphided ex situ by
various sulphiding processes; as an illustration, see "Sul-
phicat[R]: Offsite Presulphiding of Hydroprocessing Catalysts
from Eurocat" by J.H. Wilson and G. Berrebi, Catalysts 87,
Studies in Surface Science and Catalysts #38 page 393. Al-
ternatively, the sulphiding is accomplished in situ, i.e.
by using the catalyst in the oxide form to hydrocrack a hy-
drocarbon feedstock containing sulphur compounds under hy-
drocracking conditions including elevated temperature and
pressure and the presence of hydrogen.

Hydrocracking catalysts in accordance with the invention
are useful in the conversion of a wide variety of hydrocar-
bon feedstocks to a hydrocarbon product of lower average
boiling point and/or molecular weight. The feedstocks that
may be subjected to hydrocracking by the methods of the in-

vention include all mineral oils and synthetic oils (e.g.
shale oil, tar sand products etc.) and fractions thereof.
Illustrative feedstocks include straight run gas oils, vac-
uum gas oils, coker gas oils and catcracker distillates.

5   The typical hydrocracking feedstock, however, contains a
substantial proportion of components usually at least 50
percent by volume, often at least 75% by volume boiling
above the desired end point of the products, which end
point in the case of gasoline, will generally be in the

10   range of about 190°C to 215°C and in the case of middle
distillates will typically be in the range of 340°C to
425°C. Usually, the feedstock will also contain gas oil
components boiling above 285°C with highly useful results
being achievable with feeds containing at least 30 percent

15   by volume of components boiling between 315°C and 600°C.

For best results in hydrocracking, the catalyst of the in-
vention will be employed as a fixed bed of catalytic par-
ticulates in a hydrocracking reactor vessel into which hy-

20   drogen and the feedstock are introduced and passed in a
downwardly direction. Operating conditions in the reactor
vessel are chosen so as to convert the feedstock into the
desired product, which in one preferred embodiment is a hy-
drocarbon product containing a substantial proportion of

25   gasoline components boiling, for example in the 85°C to
215°C range. However, other products such as middle distil-
lates boiling in the 150°C to 425°C range may also be
highly desired, and conditions must be adjusted according
to the product (or distribution of products) desired. The

30   unconverted oil, e.g. hydrocarbons boiling at a temperature
higher than that of the middle distillate fraction may be
used for production of lube oil blending stocks, fluid

cracker feedstocks or ethylene cracker feedstock. The exact
conditions required in a given situation will depend upon
the nature of the feedstock, the particular catalyst compo-
sition utilised, and the desired product(s). In general,
5   the conditions of operation for hydrocracking will fall
into the following usual and preferred ranges.

TABLE 1

Conditions	Usual	Pre- ferred
Temperature, °C	230-455	260-430
Pressure, Mpa	4-30	5-20
LHSV, h^{-1}	0.3-5.0	0.5-3.5
H$_2$/feedstock, Nm^3/m^3	200- 2000	500- 1500

10

The foregoing Table 1 shows the suitable and preferred hy-
drocracking conditions for single stage or for each stage
of a two stage operation. It will be understood, however,
15   that the operating conditions in the two stages of the two
stage process are not necessarily identical. In fact, as
mentioned before, the primary difference in conditions in
the two hydrocracking reactor vessels of two stage opera-
tion is the presence of substantial amounts of ammonia of-
20   ten greater than about 2000 vol ppm in the first stage, and
its essential absence, i.e. less than 200 vol ppm and pref-
erably less than about 20 vol ppm in the second, allowing
for less severe conditions in the second stage. There may,
however, be yet other differences in conditions in any par-
25   ticular situation.

Based on the presently available data, the catalysts of the
invention, when compared with Y zeolite catalysts of simi-
lar NH$_3$-AI and IEC-AI, are found to be substantially more

selective for middle distillate production. These achieve-
ments and others are proven in the following examples,
which are provided for illustration purposes and not to
limit the invention as defined by the claims.

5

EXAMPLES

The key parameter in defining the zeolites are measured by
the following techniques:

10

AMMONIA TEMPERATURE PROGRAMMED DESORPTION (NH$_3$ TPD)
A 0.1 g sample of zeolite is heated in helium at 500°C for
2 hours. The pretreated zeolite is then cooled to 150°C.
The sample is then saturated at this temperature by a mix-
15   ture of 2 vol% ammonia in helium for ½ hour. The saturated
zeolite is then purged with helium for 2 to 3 hours. Imme-
diately after this period, the exit gas is directed to a
bubble flask containing 100 ml of a 0.65 N boric acid solu-
tion and 100 ml water in order to collect the desorbed am-
20   monia, while the temperature is raised to 850°C with a tem-
perature ramp of 10°C/min. The boric acid solution is then
titrated with a 0.01 N HCl solution until the pH equals
4,90. At this point the amounts of HCl added equals the
amount of NH$_3$ desorbed from the zeolite sample, and the
25   acidity is reported as mmole NH$_3$ desorbed per gram of sam-
ple after the determination.

ION EXCHANGE CAPACITY (IEC)
10 grams of zeolite are contacted three times at 25°C for a
30   period of one hour each time with a fresh aqueous ion ex-
change solution containing 10 g of NaCl per liter of solu-
tion (100 ml of solution is used for each gram of zeolite).

23

After this contact, the zeolite is contacted for one hour
with 100 ml hot pure water for each gram of zeolite (60-
70°C) in order to remove excess of sodium. The sodium con-
tent after calcination at 600°C is then determined and re-
5   ported as the ion exchange capacity.

NH$_3$ TPD ACIDITY INDEX (NH$_3$-AI)

The NH$_3$-AI is defined as the amount of mole NH$_3$/g zeolite
(measured by the NH$_3$ TPD method) of the zeolite used in the
10   catalyst support multiplied by the weight percentage of the
zeolite in the catalyst support normalised by a catalyst
support containing 1 wt% of a standard zeolite beta (CP
814E from Zeolyst International) having a specified
SiO$_2$:Al$_2$O$_3$ molar ratio of 25 and a NH$_3$-TPD of 0.90 mmole
15   NH$_3$/g zeolite (all on dry weight basis).

$$NH_3\text{-}AI = \frac{(\text{mole } NH_3/g \text{ zeolite})*(\text{zeolite content in catalyst support, wt\%})}{(\text{mmol } NH_3/g \text{ standard zeolite beta})*(1 \text{ wt\%})}$$

20

ION EXCHANGE CAPACITY ACIDITY INDEX (IEC-AI)

The IEC-AI is defined as the amount of wtppm of sodium in
25   the zeolite (measured by the IEC method) used in a catalyst
support multiplied by the weight percentage of zeolite in
the catalyst support normalised by a catalyst support con-
taining 1% of a standard zeolite beta (CP 814E from Zeolyst
International) having a specified SiO$_2$:Al$_2$O$_3$ molar ratio of
30   25 and an IEC of 18,500 wtppm sodium (all on dry weight ba-
sis).

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$$IEC\ AI\ =\ \frac{\text{wtppm sodium})*(\text{zeolite content in catalyst support, wt\%})}{(\text{wtppm sodium in standard zeolite beta})*(1\ \text{wt\%})}$$

Example 1

A catalyst was prepared by mixing 10 wt% of a commercially available zeolite beta having a specified $SiO_2:Al_2O_3$ molar ratio of about 1500, a NH_3 TPD of 0.077 mmole NH_3/g zeolite and an ion exchanged capacity (IEC) of 630 wtppm sodium with 35 wt% amorphous silica-alumina (high alumina type) and 55 wt% gamma alumina. The resulting mixture was extruded to form 1/16" extrudates. The extrudates were dried and calcined at 550°C for 2 hours in air. The calcined extrudates were impregnated with an aqueous solution containing nickel nitrate and ammonium metatungstate. The wet extrudates were dried and calcined at 550°C for 2 hours in air. The final catalyst contained 6 wt% nickel oxide (NiO) and 22 wt% tungsten oxide (WO_3) (all on dry weight basis).

Examples 2-4

The three catalysts of Examples 2-4 were prepared in the same way as in Example 1 except that other beta zeolites were used. In Example 2, a commercially available zeolite beta having a specified $SiO_2:Al_2O_3$ molar ratio of about 500, a NH_3 TPD of 0.092 mmole NH_3/ g zeolite and an IEC of 2000 wtppm sodium was used. In Example 3, a commercially available zeolite beta with a specified $SiO_2:Al_2O_3$ molar ratio of about 300, a NH_3 TPD of 0.151 mmole NH_3/g zeolite and an IEC of 2870 wtppm sodium was used. In Example 4, a commercially available zeolite beta with a specified $SiO_2:Al_2O_3$

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molar ratio of about 100, a NH$_3$ TPD of 0.236 mmole NH$_3$/g
zeolite and an IEC of 5630 wtppm sodium was used.

Example 5

5   A sample of a commercially available zeolite Y type was
steamed in 100% steam for two hours at 750°C resulting in
an NH$_3$ TPD of 0.089 mmole NH$_3$/g zeolite and an IEC of 1630
wtppm sodium. A portion of this modified zeolite Y was
mixed with 74 wt% amorphous silica-alumina (high alumina
10   type), and 20 wt% gamma alumina to obtain a mixture con-
taining 6 wt% of the modified zeolite Y. The mixture was
extruded, calcined and impregnated as in Example 1.

Example 6

15   A catalyst was prepared in the same way as described in Ex-
ample 5 except that a commercially available zeolite Y type
with a specified SiO$_2$:Al$_2$O$_3$ molar ratio of about 15, a NH$_3$
TPD of 0.118 mmole NH$_3$/g zeolite and an IEC of 2105 wtppm
sodium was used.

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Examples 7-8

Two catalysts were prepared in the same way as described in
Example 1 expect that the beta zeolite component was re-
placed by zeolite Y. In Example 7, a commercially available
25   zeolite Y type with a specified SiO$_2$:Al$_2$O$_3$ molar ratio of
about 55, a NH$_3$ TPD of 0.229 mmole NH$_3$/g zeolite and an IEC
of 5990 wtppm sodium was used. In Example 8, a commercially
available zeolite Y type with a specified SiO$_2$:Al$_2$O$_3$ molar
ratio of about 30, and an NH$_3$ TPD of 0.428 mmole NH$_3$/g zeo-
30   lite and an IEC of 9570 wtppm sodium was used.

The properties of the catalyst support with the calculated
NH₃-AI and IEC-AI of Examples 1-8 are given in Table 2. The
zeolite used in the examples have been obtained from Tosoh
Corporation Zeolyst International.

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Example 9

The catalysts prepared in Examples 1-8 were tested accord-
ing to the following conditions. Prior to testing, the
catalyst was sulphided in the presence of hydrogen and hy-
10   drogen sulphide at a temperature from 150°C to 360°C. Feed
A (properties are given in Table 3) was passed on a once-
through basis through an isothermal reactor containing
catalyst particles uniformly mixed with carborundum. The
catalyst was tested under the following operating condi-
15   tions: LHSV of 0.5-1.0 h⁻¹, total pressure 14.2 MPa, and a
hydrogen gas/feed ratio of 1500-1800 Nl/l. The temperature
of the reactor was adjusted to provide 75 wt% conversion of
the >360°C fraction in the feedstock. The temperature re-
quired to obtain the desired conversion level was from 380-
20   400°C. The selectivity to middle distillate products was
measured as the percentage fraction of the 360°C minus
product fraction boiling in the range from 160-360°C. The
conversion and selectivity were calculated from gas chro-
matograph boiling range analyses of the product according
25   to ASTM D 2887.

The results of the testing of all catalysts are given in
Table 4. The data in Table 2 and Table 4 and Figs. 1-2 show
a comparison of catalysts containing modified zeolite beta
30   versus catalysts containing zeolite Y. The catalysts of the
invention are very superior in terms of selectivity to mid-
dle distillates. The data also reveal that the catalysts

27

had excellent denitrogenation and desulphurisation activi-
ties. The pour point of the >360°C product cut as compared
with the pour point of the same fraction in the feedstock
was reduced significantly during the processing.

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Example 10

A catalyst was prepared in the same way as in Example 1
containing 10 wt% of a commercially available zeolite Y
type having a specified SiO_2:Al_2O_3 molar ratio of about 15,
10   an NH_3 TPD of 0.118 mmole NH_3/g zeolite and an IEC of 2105
wtppm sodium resulting in an NH_3-AI of 1.311 and a IEC-AI
of 1.249.

Example 11

15   A commercially available zeolite beta with a specified
SiO_2:Al_2O_3 molar ratio of about 300, an NH_3 TPD of 0.151
mmole NH_3/g zeolite and an IEC of 2870 wtppm sodium result-
ing in an NH_3-AI of 1.174 and an IEC-AI of 1.086 was mixed
with 38 wt% amorphous silica-alumina (high alumina type)
20   and 55 wt% gamma alumina to obtain 7 wt% zeolite in the
catalyst support. The mixture was extruded to form 1/16"
extrudates. The extrudates were calcined and impregnated as
in Example 1. The zeolite used in the examples have been
obtained from Tosoh Corporation Zeolyst International.

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Example 12

The catalysts prepared in Examples 10 and 11 were tested
according to the procedure given in Example 9 except that
Feed B with the properties given in Table 3 was used. The
30   zeolite used in the examples have been obtained from Tosoh
Corporation Zeolyst International.

The test of the catalyst containing zeolite Y prepared in
Example 10 with an NH_3-AI of 1.311 and an IEC-AI of 1.249
results in a selectivity to middle distillate of 69.1%. The
catalyst prepared in Example 11 containing zeolite beta

5   with an NH_3-AI of 1.174 and an IEC-AI of 1.086 results in a
selectivity to middle distillate of 71.9%.

Example 12 illustrates that the catalyst containing zeolite
beta in accordance with the present invention is clearly

10   more selective to middle distillate on a second feed than
the catalyst based on zeolite Y with similar NH_3-AI and
IEC-AI.

TABLE 2

15

ZEOLITE AND CATALYST PROPERTIES			
Exam-ple	Zeolite Type	NH_3-AI wt%	IEC-AI wt%
1	Beta	0.856	0.341
2	Beta	1.022	1.081
3	Beta	1.678	1.551
4	Beta	2.622	3.043
5	Y	0.593	0.529
6	Y	0.787	0.683
7	Y	2.544	3.243
8	Y	4.759	5.173

TABLE 3

FEED PROPERTIES

	FEED A	FEED B
Specific gravity	0.8785	0.8816
Sulphur, D-4294, wt%	0.84	0.55
Nitrogen, D-4629, wtppm	641	601
Hydrogen, D-4804, wt%	12.95	13.05
Aromatics, IP-391, wt%	12.9	15.4
Mono	5.1	4.6
Di	6.6	6.1
Tri+	30	30
Pour Point, D-5949,°C	13.79	
Viscosity @40°C, cSt		11.5
Viscosity @50°C, cSt	3.229	3.506
Viscosity @100°C, cSt		
Distillation,°C, D-2887		
IBP/5	168/26	209/274
10/20	4	308/344
30/40	296/32	366/383
50/60	6	399/413
70/80	354/37	425/437
90/95	1	451/462
FBP	387/40	489
	2	
>360°C, wt%	416/43	72.6
	2	
>360°C cut	456/47	
Pour Point, D-5949,°C	7	
Specific gravity	514	
	66.7	
	36	
	0.8869	

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TABLE 4

TEST RESULTS

Example	Feed	Selectivity to middle distillates 160-360°C	>360°C Pour Point	Product Nitrogen	Product Sulphu
1	A	73.9%	0°C	<1 wtppm	1 wtpp
2	A	73.5%	-1°C	<1 wtppm	2 wtpp
3	A	69.2%	7°C	<1 wtppm	4 wtpp
4	A	65.2%	7°C	<1 wtppm	3 wtpp
5	A	69.4%			
6	A	69.4%			
7	A	66.6%			
8	A	62.5%			

Although it should be more than clear from the previous how

5   the invention can be utilised in the industry, it can be

summarised as follows: The invention will find its use in

the petroleum refining industry, and more specifically in

those processes employed in the petroleum refining industry

that require catalysts. Catalysts prepared in accordance

10   with the invention are most usefully employed without hy-

drogenation components in such processes as catalytic

cracking, catalytic isomerisation, catalytic alkylation and

catalytic transalkylation. The catalysts of the invention

31

are most usefully employed with one or more hydrogenation
components when catalytic hydrocracking, catalytic hydrode-
nitrogenation or catalytic hydrodesulphurisation is re-
quired. The best contemplated use of the catalyst of the
5   invention is for hydrocracking of gas oils and the like to
produce midbarrel products boiling in the 150°C to 420°C
range, and for such hydrocracking the most preferred cata-
lyst comprises sulphided nickel and tungsten components on
a catalyst support consisting essentially of a modified
10   beta zeolite, silica-alumina, alumina and binder.

While particular embodiments of the invention have been de-
scribed, it goes without saying that the invention is not
limited thereto since many obvious modifications can be
15   made, and it is intended to include within this definition
any such modifications as will fall within the scope of the
appended claims.